2009

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Citation/Publisher Attribution

Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates, Atmos. Chem. Phys., 9, 1451-1463, doi:10.5194/acp-9-1451-2009, 2009.
Available at: http://dx.doi.org/10.5194/acp-9-1451-2009

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Atmos. Chem. Phys., 9, 1451–1463, 2009
www.atmos-chem-phys.net/9/1451/2009/

Atmospheric Chemistry and Physics

Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates

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Received: 16 May 2008 – Published in Atmos. Chem. Phys. Discuss.: 24 June 2008
Revised: 26 January 2009 – Accepted: 26 January 2009 – Published: 23 February 2009

Abstract. Formation of isoprene nitrates (INs) is an important free radical chain termination step ending production of ozone and possibly affecting formation of secondary organic aerosol. Isoprene nitrates also represent a potentially large, unmeasured contribution to OH reactivity and are a major pathway for the removal of nitrogen oxides from the atmosphere. Current assessments indicate that formation rates of isoprene nitrates are uncertain to a factor of 2–3 and the subsequent fate of isoprene nitrates remains largely unconstrained by laboratory, field or modeling studies. Measurements of total alkyl and multifunctional nitrates (ΣANs), NO_2, total peroxy nitrates (ΣPNs), HNO_3, CH_2O, isoprene and other VOC were obtained from the NASA DC-8 aircraft during summer 2004 over the continental US during the INTEX-NA campaign. These observations represent the first characterization of ΣANs over a wide range of land surface types and in the lower free troposphere. ΣANs were a significant, 12–20%, fraction of NO_y throughout the experimental domain and ΣANs were more abundant when isoprene was high. We use the observed hydrocarbon species to calculate the relative contributions of ΣAN precursors to their production. These calculations indicate that isoprene represents at least three quarters of the ΣAN source in the summertime continental boundary layer of the US. An observed correlation between ΣANs and CH_2O is used to place constraints on nitrate yields from isoprene oxidation, atmospheric lifetimes of the resulting nitrates and recycling efficiencies of nitrates during subsequent oxidation. We find reasonable fits to the data using sets of production rates, lifetimes and recycling efficiencies of INs as follows (4.4%, 16 h, 97%), (8%, 2.5 h, 79%) and (12%, 95 min, 67%). The analysis indicates that the lifetime of ΣANs as a pool of compounds is considerably longer than the lifetime of the individual isoprene nitrates to reaction with OH, implying that the organic nitrate functionality is at least partially maintained through a second oxidation cycle.

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1 Introduction

Global isoprene emissions are estimated at 440–660 Tg/yr (Guenther et al., 2006), more than the estimated sum of all anthropogenic non-methane organic compounds (130 Tg/yr) (Bey et al., 2001; Guenther et al., 1995; Piccot et al., 1992). Isoprene emissions and subsequent chemistry are thus major influences on tropospheric chemistry with notable

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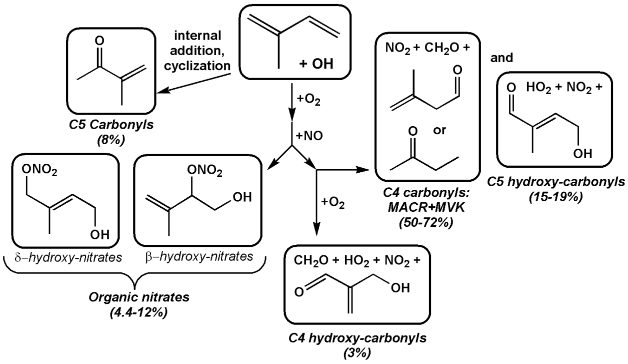

Fig. 1. Examples of each class of OH-initiated isoprene oxidation products observed (in the presence of NO_x) and the ranges of observed yields.

effects on ozone (O_3), secondary organic aerosol, the hydroxyl radical (OH) concentrations and on the NO_y budget (NO_y=NO+NO_2+HNO_3+peroxy nitrates (ΣPNs)+alkyl and mulitfuctional nitrates (ΣANs)+other minor species) (Atkinson et al., 1983; Fiore et al., 2005; Houweling et al., 1998; Ito et al., 2007; Wu et al., 2007). Recent experiments and calculations show that there is still much to be learned about the chemistry of isoprene and its oxidation products. For example, chamber experiments now show that isoprene photooxidation can be an important source of SOA (Boge et al., 2006; Kroll et al., 2005; Lee et al., 2006) consistent with the implications of field observations of tetrols with an isoprene backbone (Claeys et al., 2004) in the aerosol phase.

Uncertainties in the gas phase chemistry remain as well. Analyses of field measurements imply that the reaction of isoprene hydoxyperoxy radicals with HO_2 is not an effective HO_x chain termination step (Thornton et al., 2002) and there are several studies where observed OH significantly exceeds model calculations when isoprene is present (Kuhn et al., 2007; Lelieveld et al., 2008; Ren et al., 2003; Tan et al., 2001). In particular, we note that there are no laboratory experiments in which a complete carbon balance for the oxidation of isoprene by OH, O_3 or NO_3 have been reported. We focus here primarily on the OH-initiated pathway and Table 1 summarizes the findings of past product studies.

Photooxidation of isoprene is initiated by the addition of OH Reaction (R1), and then O_2 Reaction (R2), resulting in the formation of six chemically distinct unsaturated hydroxyperoxy radicals.

$$C_5H_8 + OH \rightarrow C_5H_8(OH) \quad \text{(R1)}$$

$$C_5H_8(OH) + O_2 \rightarrow C_5H_8(OH)O_2 \quad \text{(R2)}$$

The reactions of these peroxy radicals with NO have two product channels. The dominant channel, Reaction (R3a), propagates the HO_x and NO_x catalytic cycles with production of NO_2 and an alkoxy radical which rapidly undergoes subsequent reactions while the minor channel, Reaction (R3b), results in production of a stable unsaturated hydroxynitrate.

$$C_5H_8(OH)O_2 + NO \rightarrow C_5H_8(OH)O + NO_2 \quad \text{(R3a)}$$

$$C_5H_8(OH)O_2 + NO \rightarrow C_5H_8(OH)ONO_2 \quad \text{(R3b)}$$

Examples of each class of the observed products from Table 1 are shown in Fig. 1. The more recent studies have found higher combined yields of methacrolein (MACR) and methyl vinyl ketone (MVK) than previously reported (Karl et al., 2006; Sprengnether et al., 2002), and appreciable yields of C5 carbonyls and hydroxy-carbonyls have been observed (Baker et al., 2005; Zhao et al., 2004). A number of studies have reported small (<5%) yields of 3-methylfuran (Atkinson et al., 1989; Lee et al., 2005; Sprengnether et al., 2002; Tuazon and Atkinson, 1990b) but there is some controversy over whether this is a primary oxidation product or a secondary reaction product of the C_5 hydroxycarbonyls (Francisco-Marquez et al., 2005; Zhao et al., 2004). Taken in combination, these experiments approach carbon balance and indicate that the nitrate yield is likely not more than 12%. Studies in which the nitrate yield was examined directly report values that range from 4.4 to 12% (Chen et al., 1998; Patchen et al., 2007; Sprengnether et al., 2002; Tuazon and Atkinson, 1990b).

Uncertainties regarding the products of the reaction of isoprene hydroxyperoxy radicals with NO are important because of their effects on the NO_y budget. The resulting uncertainties in the NO_y budget propagate to uncertainty in spatial patterns of O_3 and OH concentration as well as the spatial patterns of nitrogen deposition. These uncertainties also affect predictions of the response of O_3 and presumably SOA to changes in isoprene emissions (as will likely occur in a warmer climate). For example, Wu et al. (2007) show that increasing the production rate of isoprene nitrates (INs) in a global model by a factor of three (within the currently established range of uncertainty) decreases global tropospheric ozone production by 10%.

IN production is important to the extent that the fate of NO_2 radical sequestered in the organic nitrate is different than that of free NO_2. Possible fates that have been discussed include (1) reaction of IN with O_3, OH, or NO_3 to produce (a) a more complex organic nitrate or (b) NO_2 (Giacopelli et al., 2005; Grossenbacher et al., 2001; Paulson and Seinfeld, 1992; Paulson, 1992), (2) removal from the atmosphere by dry or wet deposition (Giacopelli et al., 2005; Horii et al., 2004; Rosen et al., 2004; Shepson et al., 1996; Treves and Rudich, 2003; von Kuhlmann et al., 2004) or (3) incorporation into aerosol (Ervens et al., 2008; Kroll et al., 2005; Ng et al., 2007) with subsequent liquid phase chemistry.

Shepson and colleagues are the only group that has reported field measurements of specific IN isomers. They use GC to isolate the specific compounds and thermal dissociation followed by luminol detection of NO_2 to observe them

Table 1. Percentage yields of products observed in OH-initiated isoprene oxidation studies.

Reference Product	1	2	3	4	5	6	7	8	9
MVK	29(7)	36(4)	32(5)		44(6)	55(6)		41(3)	
MACR	21(5)	25(3)	22(2)		28(4)	(MAC+MVK)		27(3)	
Organic Nitrates	8–14			4.4	8–12				7
C5 hydroxy-carbonyls						19(6.1)	15		
C4 hydroxy-carbonyls						3.3(1.6)			
C5 carbonyls						8.4(2.4)			
Carbon accounted for	58–66	61	55	4.4	80–84	86	15	68	7

1 = Tuazon et al. (1990), 2 = Paulson and Seinfeld (1992), 3 = Myoshi et al. (1994), 4 = Chen et al. (2002), 5 = Sprengnether et al. (2002), 6 = Zhao et al. (2004) 7 = Baker et al. (2005), 8 = Karl et al. (2006), 9 = Patchen et al. (2007)

(Giacopelli et al., 2005; Grossenbacher et al., 2001, 2004). INs were ∼10 ppt at a site in Michigan and ∼115 ppt at a site in Tenessee. First-generation INs were observed to be ∼5% of NO_y at both sites. These results and the differences between the two sites have been interpreted to show that INs are important in reactive nitrogen cycling but that their abundance is strongly impacted by both NO_x loadings and photochemical processing. Giacopelli et al. (2005) conclude that, due to short lifetimes of first-generation INs to further oxidation and/or deposition, more highly oxidized derivatives of INs are likely also important and that further understanding of secondary chemistry and loss processes is needed.

In this paper, we describe observations of ΣANs from the NASA DC-8 aircraft over the Eastern US during the INTEX-NA campaign in the summer of 2004. In this study, ΣANs were measured by thermal decomposition followed by detection of NO_2 with laser-induced fluorescence, described in detail below, which detects all compounds of the form $RONO_2$ (where R represents a hydrocarbon) regardless of the identity of R. With respect to detection of INs, this non-specificity means that the technique is equally sensitive to all six first-generation isomers as well as any subsequent oxidation products that retain the nitrate functional group and that the measurement represents the sum of all of these compounds as well as any other alkyl or multifunctional nitrates that may be present. Note that this technique would be doubly sensitive to dinitrate compounds as thermal dissociation would result in production of two NO_2 molecules but, as discussed below, dinitrates are expected to be a small fraction of the observed signal. These are the most spatially extensive measurements of ΣANs to date and constitute the first observations of ΣANs in the free troposphere. In a first manuscript describing these observations, Horowitz et al. (2007) compared the aforementioned measurements to the output of a chemical transport model (MOZART), showing that model results within the continental boundary layer could be forced into agreement with observations through: (1) setting the branching ratio for IN production at the low end of the laboratory measurements (4%), (2) limiting conversion to non-nitrate species following reaction with O_3 or OH to 40% and (3) assuming fast deposition. Here we expand this analysis by isolating measurements where isoprene oxidation by OH in the presence of NO_x is unambiguously the dominant source of ΣAN which we then use to investigate factors controlling the production and the removal of molecules from the total nitrate pool and examine correlations of ΣANs with other products of isoprene oxidation.

2 Methods

NO_2, ΣPNs and ΣANs were measured using the Berkeley thermal dissociation-laser induced fluorescence technique (Day et al., 2002; Thornton et al., 2000). Briefly, gas is pulled simultaneously through four channels, one for each class of compounds above and one used to evaluate inlet transmission of HNO_3. Each channel consists of a section of heated quartz tube followed by a length of PFA tubing leading to a detection cell where NO_2 is measured using laser-induced fluorescence. Due to differing X-NO_2 bond strengths, ΣPNs, ΣANs and HNO_3 all thermally dissociate to NO_2 and a companion radical at a characteristic temperature. The ambient channel measures NO_2 alone, the second channel (180°) measures NO_2 produced from the dissociation of ΣPNs in addition to ambient NO_2 so the observed signal is NO_2+ΣPNs, the third channel (380°C) measures NO_2+ΣPNs+ΣANs, and the last channel (580°C) measures NO_2+ΣPNs+ΣANs+HNO_3. Concentrations of each class of compound correspond to the difference in NO_2 signal between two channels set at adjacent temperatures. The difference in NO_2 signal between the 180°C and the 380°C channel, for example, is the ΣANs mixing ratio. The instrument deployed for INTEX-NA had one inlet with a heated tip and immediate introduction to heated quartz tubes for detection of ΣANs and HNO_3 and one inlet with an unheated tip and introduction to an additional heated quartz tube for detection of ΣPNs and an ambient temperature channel for detection of NO_2.

Ambient NO_2 and NO_2 produced by thermal dissociation was observed by laser-induced fluorescence as described in detail by Thornton et al. (2000). Briefly, a tunable dye laser is pumped at 7 kHz by a Q-switched, frequency doubled Nd^{+3}YAG laser. The incoming gas is cooled through the use of a supersonic expansion (Cleary et al., 2002) and the dye laser, utilizing Pyrromethene 597 in isopropanol, was tuned to an isolated rovibronic feature of jet-cooled NO_2 at 585 nm. The dye laser frequency was held for 20 s at the peak of this strong resonant feature and then for 5 s at an offline position in the continuum absorption. The ratio of the peak to background fluorescence of the chosen feature is 10 to 1 at 1 atm and the difference between the two signals is directly proportional to the NO_2 mixing ratio. The laser light is focused through two multi-pass (White) cells in series and the red-shifted fluorescence is detected using a red-sensitive photomultiplier tube (Hamamatsu). Fluorescence counts are collected at 5 Hz, scattered light at wavelengths less than 700 nm is rejected by band-pass filters and time-gated detection is used to eliminate prompt noise. We observe a strong dependence of NO_2 fluorescence on the external pressure. We calibrate the NO_2 LIF instrument at a series of altitudes and interpolate calibration constants between these points using an empirical pressure correction determined by direct measurement of the NO_2 pressure dependence from a standard NO_2 addition during a test-flight. Calibrations were performed at least once every two hours during a level flight leg using a 4.7 ppm NO_2 reference gas with a stated certainty of $\pm$5%. The reference gas was compared to a library of standards in lab both before and after the campaign. The individual standards are compared on a regular basis (about every 6 months) to ensure stability and highlight when a given tank has degraded. These standards have been observed to remain stable for up to 5 years and to be accurate at atmospherically relevant mixing ratios to within 1% (Bertram et al., 2005).

The instrument deployed for INTEX-NA had two detection cells. Cell 1 sampled either the ambient or the 380°C channel while cell 2 sampled either the 180°C or the 580°C channel. The direction of flow into the cell was controlled using a three-way valve and a bypass pump was used to maintain flow in the non-sampled channel. Cell 1 sampled the unheated NO_2 channel 75% and the 380°C channel (ΣANs) 25% of the time. Cell 2 sampled the 180°C and the 580°C channels 50% of the time each. During INTEX-A, the 200C ($NO_2+\Sigma$PNs) and 380°C ($NO_2+\Sigma$PNs+ΣANs) channels were sampled sequentially and the signal in the 200°C channel was interpolated across the 20 s interval when the 380°C channel was sampled to calculate the ΣANs concentration. Thus for every 2 min duty cycle there were three 20 s average measurements of NO_2, two 20 s average direct measurements of ΣPNs, one 20 s average direct measurement of HNO_3 and one 20 s average measurement of ΣANs using interpolated ΣPNs values. The uncertainty of the ΣANs measurement depends strongly on the amount and variability of NO_2 and ΣPNs. ΣANs were not reported above 4 km because above that point ΣANs levels were routinely an order of magnitude smaller than the underlying $NO_2+\Sigma$PNs signal and could not reliably be distinguished from the temporal variation between subsequent measurements of the 200C channel.

The TD-LIF measurement of HNO_3 has been shown to be the sum of aerosol and gas-phase HNO_3 (Fountoukis et al., 2007) and we expect aerosol phase organic nitrates to behave similarly. While a direct intercomparison of the ΣANs measurement has not been published, we have sampled pure isoprene nitrates (synthesized by wet chemical methods in the laboratory) in air, and observed the signals in the non-nitrate channels of the TD-LIF to be zero (indicating that the nitrates are not dissociating in the other temperature channels) and the magnitude of the signal to match both the calculated concentration and a PTR-MS measurement to within 10% (Perring et al., 2009). Additionally, we have reported field observations of the thermal decomposition of ambient samples expected to have significant isoprene nitrate influence and shown a correspondence between predicted and observed temperature dependence (Day et al., 2002; Murphy et al., 2006).

HNO_3 was measured by the University of New Hampshire with a mist chamber followed by ion chromatography (Dibb et al., 1994) and by Caltech using Chemical Ionization Mass Spectrometry (CIMS) (Crounse et al., 2006; Huey et al., 1996, 2004). Hydrocarbons were measured by UC Irvine using gas chromatography of whole air samples (Colman et al., 2001). Oxygenated volatile organic carbon species (methyl-ethyl-ketone, methanol, ethanol, acetone and acetaldehyde collectively referred to, when combined with CH_2O, as oxidized volatile organic carbon or OVOC) were measured by NASA Ames using gas chromatography (Singh et al., 1999). NO (Penn State) and O_3 (NASA Langley) were measured through chemiluminesence. OH and HO_2 were measured by laser-induced fluorescence by Penn State (Faloona et al., 2004). CH_2O was measured by NCAR using tunable diode laser absorption spectroscopy (TD-LAS) (Fried et al., 2003) and by the University of Rhode Island using an enzyme-derivatization fluoresence technique following collection in an aqueous medium (Heikes, 1992).

The University of Rhode Island measurement was systematically $\sim$35% lower than the NCAR measurement and this discrepancy remains unresolved as of the preparation of this manuscript. For the purposes of this analysis we use the average of the two measurements when both are available. Despite the absolute disagreement, the two measurements are very highly correlated so, to increase data coverage when only a single measurement is available, we scale that measurement up or down by the appropriate amount to arrive at what the mean of the two would have been had both been available.

The INTEX-NA campaign has been described in detail (Singh et al., 2006). It consisted of 18 flights over the continental US east of 40° W and between 30 and 50° N during July and August of 2004 with extensive vertical profiling.

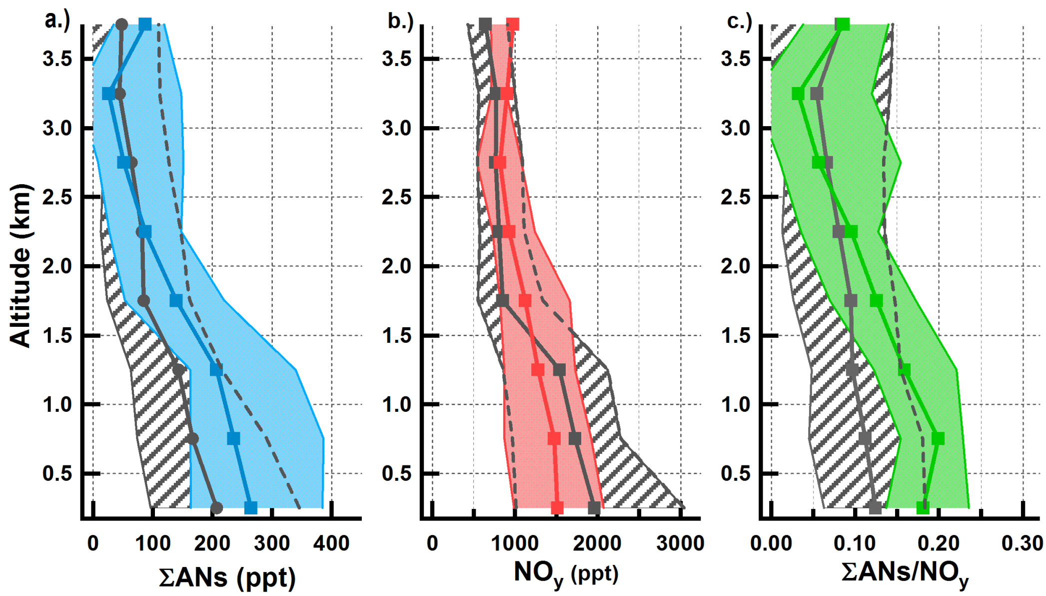

Fig. 2. Medians and interquartile ranges of **(a)** ΣANs, **(b)** NO_y (NO_y=NO+NO_2+ΣPNs+ΣANs+HNO_3), and **(c)** ΣANs/NO_y. The colored points and shading are regions where isoprene exceeded 500 ppt in the planetary boundary layer below the measurement. The gray lines represent all continental data.

The data used in this analysis are a subset of points taken over the continental US and are from a 1-min merged data set, available as described at http://www-air.larc.nasa.gov. The time resolution of the UCI hydrocarbon data was sometimes longer than 1 min in which case the concentrations observed in the sample are reported for each of the minutes spanned by the collection time.

3 Results and discussion

3.1 ΣAN and NO_yvertical profiles

Figure 2 shows vertical profiles of ΣANs, NO_y and ΣANs/NO_y. As shown in panel 2c, the median ΣANs component of NO_y was ∼12% at the surface over the continental US when all continental data points are considered. When boundary layer isoprene exceeded 500 ppt (∼14% of continental data below 2 km) the median ΣANs component of NO_y at the surface increased to 18%. ΣANs are a larger fraction of NO_y when isoprene is high (>500 ppt) than in the ensemble of observations because of both a higher concentration of ΣANs (250 ppt vs. 200 ppt) and a reduced overall NO_y concentration (1500 ppt vs. 2000 ppt). The lower boundary layer NO_y concentration when isoprene is high is due to both lower NO_2 (380 ppt vs. 600 ppt) and lower HNO_3 (820 ppt vs. 1050 ppt) and indicates that the regions of highest biogenic activity were generally removed from anthropogenic NO_x sources.

There is large spatial variability in isoprene concentrations and, while we would expect this variability to be reflected in observed ΣANs concentrations, the variability in isoprene observed aboard the DC8 is the result of not only spatial variability but also variability in elapsed time between emission and sampling. As a result we do not observe a simple correlation between isoprene and ΣANs (or CH_2O) but the comparison between the vertical profiles when isoprene is high and when it is not qualitatively supports the conjecture that production of ΣANs is closely associated with isoprene. The lifetime of isoprene with respect to OH oxidation was well under an hour in the summertime continental boundary layer of the US and we expect significant amounts of the products of isoprene oxidation to persist long after the consumption of the initial isoprene. Some of the high ΣANs and CH_2O points also coincide with high isoprene but ΣANs and CH_2O were often both high when isoprene was at the detection limit. We interpret this to imply that we were in an isoprene-impacted region where all of the isoprene had reacted away but the products remained for a more sustained period of time. In the present discussion, we are less interested in the amount of isoprene present at any given time and location and more interested in the amount of isoprene oxidation that has occurred prior to sampling by the DC8. The major products of isoprene oxidation are methacrolein (MACR), methylvinyl ketone (MVK) and CH_2O. Measurements of MACR and MVK were unavailable so we take CH_2O as our best indicator of isoprene oxidation.

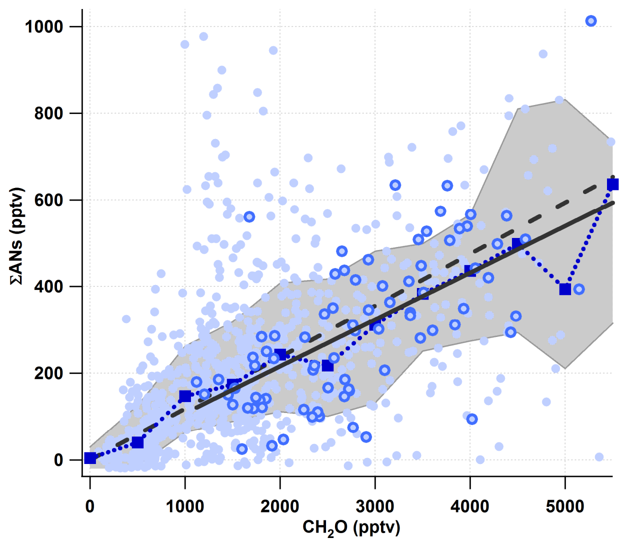

Fig. 3. Observed correlation between ΣANs and CH_2O; light blue points represent all continental points below 1 km, points outlined in dark blue represent continental points below 1 km that had isoprene >500 ppt, Dark blue squares and dotted lines are the median ΣAN concentrations in 500 ppt CH_2O bins and the shaded grey area is the interquartile range of the data. The black dashed line is the best fit of all data points (slope=0.119, intercept fixed at 0, r^2= 0.55). The solid black line is the best fit of for high isoprene points (slope=0.108, intercept fixed at 0, r^2=0.68).

3.2 ΣANs v CH_2O correlations

As indicated in Fig. 1, both ΣANs and CH_2O are first generation stable reaction products of isoprene oxidation in the presence of NO_x. If isoprene were the only or the primary source of these two compounds, then we would expect a strong correlation between them in ambient samples. Figure 3 shows that ΣANs and CH_2O are indeed correlated with a fit to the observations giving ΣANs=0.119×CH_2O, R^2=0.55 and a correlation using only high isoprene (>500 ppt) data gives a similar slope of 0.108 and an R^2 of 0.68. Calculations using the observed suite of VOC, OVOC and radical species (discussed in detail below) indicate that isoprene is the primary source of INs. If a significant portion of isoprene oxidation happens in the absence of NO_x, this would constitute a formaldehyde source but not an IN source and would weaken the correlation. In the present data set 90% of the continental data below 1 km had more than 500 ppt of NO_y indicating the predominance of NO_x-impacted airmasses and the vast majority of points that did have less than 500 ppt of NO_y also had less than a ppb of CH_2O. The effects of CH_2O from low-NO_x isoprene oxidation will thus be most pronounced in the region of the ΣANs-CH_2O correlation that has the least impact on the slope (i.e. low CH_2O, low ΣANs). We use a formaldehyde yield of 70% (Karl et al., 2006) as a transfer standard to determine the nitrate formation yield. If we were to ignore loss processes and atmospheric mixing, and if we were observing only the first-generation products of isoprene oxidation, the slope of the ΣANs/CH_2O correlation observed during INTEXA (0.119 ΣANs per CH_2O) would imply a nitrate branching ratio of ∼8.3%:

$$\left[\frac{\sum \text{ANs}}{\text{CH}_2\text{O}}\right] \times [\text{CH}_2\text{O formation ratio}] = [\text{INs formation ratio}]$$

In what follows, we examine the role that mixing and removal processes play in modifying the ΣANs-CH_2O correlation and the constraints that this correlation can place on IN yield, lifetime and NO_x recycling efficiency.

3.3 Investigation of ΣAN and CH_2O sources

Recently, satellite measurements of CH_2O have been used to infer isoprene emissions (Holzinger et al., 2007; Millet et al., 2006; Palmer et al., 2007). Palmer et al find that isoprene is responsible for 32% of the global CH_2O production potential and that it drives the CH_2O variability almost entirely as the other main precursors (methane and methanol) are significantly longer lived and well mixed and thus simply raise the formaldehyde background. Also, since we are focusing specifically on the lower troposphere where isoprene originates we would expect the contribution from isoprene to be even higher than when averaged over the entire tropospheric column.

Measured OH combined with OH production and loss rates calculated from measured species indicate that we are likely missing only 10–30% of the total reactivity and that the suite of measured VOC's is reasonably complete. The mean ΣANs contribution to OH reactivity can be estimated at 0.45 s^{-1} or roughly 18% of the total OH loss rate assuming a rate constant typical of addition to a double bond (6.92×10^{-11} cm^3/molecs/s) as would be the case for an isoprene derived nitrate, discussed in more detail below. This is likely an upper limit to the actual reactivity for ΣANs as any more highly oxidized compounds that lack a double bond would be significantly less reactive. The relative contributions to OH loss at the lowest altitude (0–0.5 km) are shown graphically in the left panel of Fig. 4a. For the entire data set, 24% of the reactivity at the surface is due to isoprene (comparable to the reactivity due to CO) while that due to the sum of all other non-methane hydrocarbons is only 4%. For the high isoprene data 53% of the reactivity at the surface is due to isoprene and that due to other NMHC is approximately 4%. CO is the second most important (∼14%) OH sink for the high isoprene case as well. The mean reactivity due to the sum of the measured OVOC was ∼25% of the total in the full data set and 15% in the high isoprene data. Formaldehyde alone accounted for about half of the OVOC reactivity with the remaining compounds each contributing small (<5%) amounts.

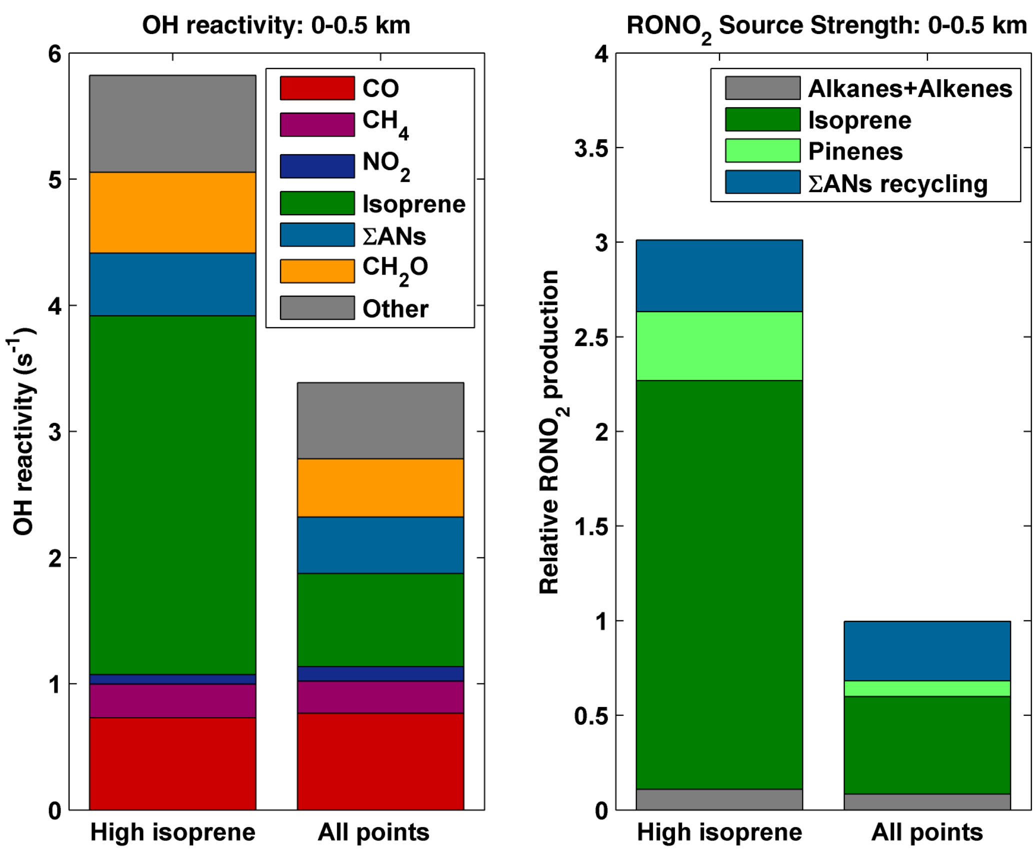

Fig. 4. **(a)** Calculated mean contributions to OH reactivity when isoprene is high and in the bulk data. "Other" includes all measured non-methane hydrocarbons other than isoprene as well as acetone, acetaldehyde, MEK, methanol, ethanol, HNO_3, peroxides and HO_x self-reactions. **(b)** Calculated mean contribution to the ΣANs signal for high isoprene points and the bulk data normalized to the bulk data ΣANs production, using an isoprene branching ratio of 4.4% and a recycling efficiency of 80%.

The relative reactivities of measured hydrocarbons were weighted by their nitrate branching ratios to calculate a fractional contribution to the ΣANs signal resulting from each precursor. Nitrate branching ratios for non-isoprene alkanes were taken from Atkinson et al (Atkinson et al., 1982; O'Brien et al., 1998), for alkenes from O'Brien et al. (1998) and that for isoprene was assumed to be 4.4% (Chen et al., 1998; Horowitz et al., 2007). Nitrates derived from MACR and MVK, VOC precursors which were not measured, are not included in the calculation, however their nitrate branching ratios are expected to be small (Tuazon and Atkinson, 1990a). Hydrocarbon measurements that were below the detection limit were assumed to be 0 but parallel calculations were performed assuming levels equal to the lower limit of detection (typically 5 ppt) and results were not markedly different. The results of this calculation are shown graphically in the right panel of Fig. 4b. Using means of all continental data below 0.5 km, about three quarters of ΣANs are predicted to be isoprene derived and, in the specifically high isoprene points, the calculated mean contribution increases to 82%. If, instead, we use a 12% branching ratio the isoprene source of ΣANs exceed 90% in the full data set and 93% in the high isoprene case. Also, the distribution shown in Fig. 4 represents the mean of the instantaneous reactivity at the time of observation and, as such, will underemphasize the importance of short-lived compounds that have been appreciably consumed prior to sampling. Isoprene itself is the shortest lived of the observed hydrocarbons so it may be an even larger fraction of the ΣANs source than indicated by the calculation.

There is a potential source of isoprene-derived ΣANs from the nighttime oxidation of isoprene by NO_3 but, as they are primarily formed just after sunset and are expected to have short lifetimes to both deposition (at night) and oxidation (after sunrise), we expect them to impact daytime concentrations only minimally. There is also an unaccounted for ΣANs source from unmeasured terpene compounds, which we expect to be no stronger than that due to alpha and beta-pinene which account for only a small fraction (10%) of ΣANs.

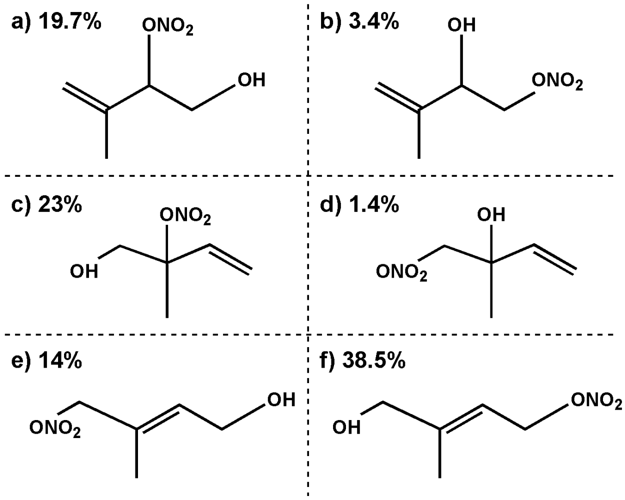

Fig. 5. Relative abundances of the six possible first-generation INs as calculated based on formation pathway branching ratios presented in Giacopelli et al. (2005).

In summary, given a reasonably complete suite of VOC measurements and using a nitrate formation branching ratio on the low end of the published range, we calculate that isoprene is the primary source of both ΣANs and CH_2O within the summertime boundary layer of the continental US. This is especially true for CH_2O that is observed to be well above the background. This fact allows us, in what follows, to use the ΣANs-CH_2O correlation to constrain the isoprene oxidation mechanism and in the fate of isoprene oxidation products.

3.4 Atmospheric processing of isoprene nitrates

In addition to constraining the sources of ΣANs and CH_2O, our interpretation of this correlation requires that we are able to account for the impacts of atmospheric mixing, chemical conversion of nitrates to other forms of NO_y, loss of CH_2O and deposition. Taking the mixing term first, we observe that the free tropospheric (above 1 km) levels of ΣANs and CH_2O, while smaller in magnitude, lie along a similar ΣANs-CH_2O correlation line (slope=0.114, R^2=0.54) to that observed from 0–1 km in the boundary layer (shown in Fig. 3). Although higher precision observations would likely be able to resolve some effects of mixing, overall the observations indicate that there is not a pool within the regional atmosphere that has concentrations that can alter the ΣANs/CH_2O ratio by mixing.

The remaining factors to assess are chemistry and deposition. The CH_2O lifetime to the sum of photolysis and OH oxidation was approximately 3 h, calculated from observed OH and J values, in the planetary boundary layer during INTEX-NA. Deposition is not expected to significantly shorten its lifetime. Estimation of the ΣAN lifetime requires consideration of the composition of ΣANs and speciation among different INs, Fig. 5 shows the six possible IN isomers and their relative percentage yields as calculated by Giacopelli et al. (2005). These six isomers are each predicted to have different rate constants for reaction with OH, O_3 and NO_3. To arrive at an overall estimate we calculate effective rate constants for the suite of INs weighted according to the product yields of the individual isomers (taken from Giacopelli et al., 2005) and derive 6.92×10^{-11} cm^3/molecs/s for OH+IN, and 2.18×10^{-16} cm^3/molecs/s for O_3+IN, neglecting the effects of daytime NO_3. Using observed mean 0–1 km concentrations of OH (3.9×10^6 molecs/cm^3) and O_3 (49 ppb), the lifetime of INs to OH is about 60 min and to O_3 is about 65 min, giving a combined oxidative lifetime of about 32 min.

The rate constants for OH+IN are based on structure-reactivity relationships as outlined in Kwok and Atkinson (1995), who show that their methods replicate known rate constants to within a factor of 2. The rate constants for O_3+IN are assumed to be similar to the analogously substituted double bonds in non-nitrate hydrocarbons for which there are measured rate constants. The 1,4 isomers (internal C=C bonds) are taken from Atkinson 1997) and other isomers (terminal C=C bonds) from Grosjean and Grosjean (1996). Giacopelli et al. (2005) find that the calculated O_3 rate constants are likely an overestimation. If we reduce the O_3+IN rate constant by half and leave the OH+IN rate constant as calculated above the combined oxidative lifetime is 40 min rather than 32. Given the uncertainties in these rate constants, we estimate the uncertainty in our overall calculated oxidative lifetime to be a factor of 2. If the deposition velocity (v_d) of INs were equal to that of HNO_3 (4 cm/s; Hauglustaine et al., 1994), the lifetime to deposition in a 1 km boundary layer would be given by:

$$\left[\frac{\text{B.L. Ht (km)}}{v_d}\right] = \left[\frac{1\text{ km}}{\left(4\frac{\text{cm}}{\text{s}}\times 3600\frac{\text{s}}{\text{h}}\times 10^{-5}\frac{\text{km}}{\text{cm}}\right)}\right] = 7\,\text{h}$$

Thus the overall lifetime is determined by the instantaneous lifetime to oxidation. Although these reactions unambiguously result in production of new chemicals, it is not clear from previous laboratory experiments whether the products of IN oxidation are still ΣANs or whether they release the nitrogen in the form of HNO_3 or NO_2.

Figure 6 shows a possible mechanism and products resulting from the OH oxidation of one of the six possible IN isomers (for a complete reaction scheme for the production of INs see Sprengnether et al., 2002). Pathway 1 proceeds via H-abstraction by OH and regenerates NO_2 from the nitrate. Pathway 2 proceeds via addition of OH to the double bond to produce a peroxy radical that reacts subsequently. For simplicity, we show here the more likely of two possible peroxy radical intermediates and products only of its reaction with NO. The scheme is representative but not comprehensive and products from the other radical isomer or from reactions of the radical with something other than NO would be different. Pathway 2a shows an alkoxy radical decomposition that

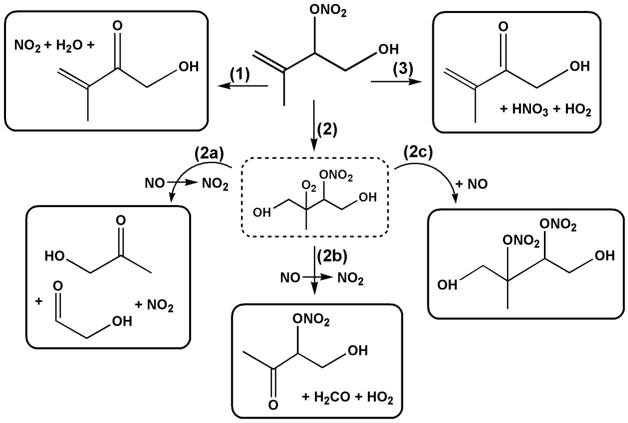

Fig. 6. Possible OH oxidation products for one of the IN isomers.

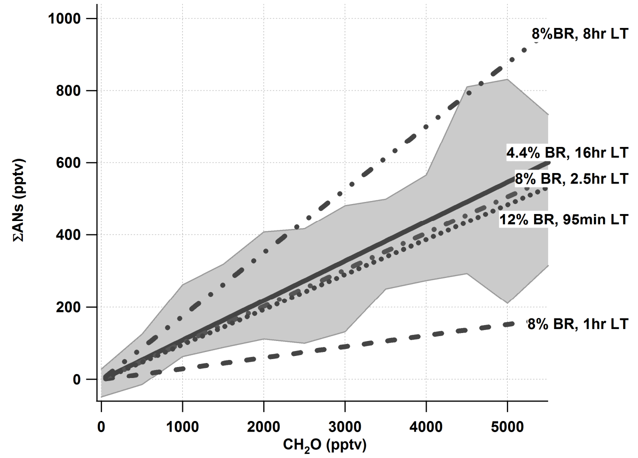

Fig. 7. As in Fig. 2, the shaded area is the interquartile range of all continental data below 1 km. Lines represent the expected correlation after 2 h of aging for various nitrate branching ratios and ΣAN lifetime combinations. From the bottom up: an 8% branching ratio and 1hr lifetime (dashed), a 12% branching ratio and 95 min lifetime (dotted), an 8% branching ratio and 2.5 h lifetime (dash-dot), a 4.4% branching ratio and 16 h lifetime (solid) and an 8% branching ratio and 8 h lifetime (dor-dot-dash).

produces NO_2 from the nitrate. Pathway 2b shows decomposition resulting in a stable mononitrate and formaldehyde. Pathway 2c produces a dinitrate and is expected to be a minor pathway but is interesting in that it results in sequestration of additional NO_x. Pathway 3 proceeds via OH addition to the nitrate group to produce HNO_3. Ozonolysis of INs could produce a similarly complex mixture of multifunctional nitrates, aldehydes and ketones (Giacopelli et al., 2005). The products of these reactions, however, are unknown and model treatment of them varies widely. Oxidation constitutes a loss process for ΣANs only if INs are converted into something that is no longer a nitrate such as HNO_3 or NO_2 (via pathways 1, 2a or 3 in Fig. 6 for example). If OH+IN reactions result simply in more functionalized nitrates, then the reaction represents a renaming but not a loss from the pool of ΣAN compounds (pathway 2b in Fig. 6). If, for example, 10% of reactions with OH lead to NO_2 production while the other 90% retain the nitrate functional group but change the identity of the parent molecule, then the effective lifetime to loss by reaction with OH would be an order of magnitude longer (10 h) than the lifetime of an individual IN. Pathway 2c is expected to be minor as the nitrate branching ratio for the intermediate peroxy radical should be no higher than for isoprene itself. We would expect less than 5% of ΣANs to be di-nitrates.

Figure 7 shows calculations of the ΣANs/CH_2O correlation for a range of ΣANs lifetimes (45 min to 20 h) assuming an initial IN yield of 8% which is in the middle of the currently published range of branching ratios. We also show calculations for a lifetime of 95 min and a 12% IN branching ratio and a lifetime of 16 h and a 4.4% branching ratio. It should be noted here that the ΣAN lifetimes shown have been calculated relative to that for CH_2O so that we would expect deviations of OH or O_3 from the mean values to result in scatter but not in a change in the overall slope expected for a given lifetime. ΣAN lifetimes of $<$1 h (or less than 1/3 that of CH_2O), which would indicate loss of nitrate functionality under oxidation by either OH or O_3, are inconsistent with the observed correlation. Unless the estimate of the OH and O_3 rate constants (6.92×10^{-11} molecs$\times$cm^{-3}s^{-1} and 2.18×10^{-16} molecs$\times$cm$^{-3}\times$s^{-1}) are in gross error (considerably more than a factor of two), this indicates that some significant fraction of IN oxidation reactions transform one nitrate into another and supports an IN branching ratio on the mid to high end of the published range. In support of this, results from a recent smog chamber study by Paulot et al. (2008) indicate an 11.2% overall branching ratio for the formation of first generation nitrates but that lifetimes and fates of these nitrates varying widely among the different isomers. The observed correlation between ΣANs and O_3 is most consistent, however, with a nitrate branching ratio that is on the low end of the 4.4–12% range (see Horowitz et al., 2007 for a graphical depiction).

If the initial nitrate production ratio is 8% then a lifetime of ∼2.5 h provides a reasonable fit of the data. Such a lifetime indicates about a 79% rate of nitrate recycling for IN oxidation reactions. Note that this is not a unique solution. We can fit the data equally well if the initial nitrate production ratio from isoprene oxidation is 12% and the IN lifetime is ∼1.5 h (an implied recycling of 67%) or if the branching ratio is 4.4% and the lifetime is ∼16 h (an implied recycling of 97%). Paulot et al. (2008) report a weighted average of 64% recycling of nitrate functionality for the first generation nitrates. Even if the O_3+IN rate constant were overestimated by a factor of 2, the observed correlation would still imply at least 50% nitrate recycling for the 12% branching ratio case, 73% recycling for the 8% branching ratio case and 96% for the 4.4% branching ratio case. If the rate constants were both underestimated by a factor of 2 and the lifetime of IN to oxidation were on the order of 15 min rather than 32 as we have calculated, that would imply a recycling rate over 80% for all conceivable branching ratios.

Formation of HNO_3 is commonly thought to be the primary mechanism for removal of reactive nitrogen from the atmosphere. Hydroxy nitrates, of which INs are a subset, have high Henry's law coefficients ($\sim 6\times10^3$ M/atm (Shepson et al., 1996) as compared to 2.1×10^5 M/atm for HNO_3; Lelieveld and Crutzen, 1991) and may therefore represent a similarly permanent NO_x termination event and be a removal pathway for nitrogen that competes with that of HNO_3 (Munger et al., 1998; Shepson et al., 1996). ΣANs were $\sim$23% of HNO_3 in the full data set and more than 35% of HNO_3 for the high isoprene points. Thus if INs deposit as rapidly as HNO_3, then 1/5 to 1/4 of total N deposition (defined here as HNO_3+IN deposition) is via isoprene nitrates.

4 Conclusions

Extensive measurements of ΣANs were made over the summertime continental US and they were observed to comprise an important (12–20%) part of the NO_y budget. The ΣANs fraction of NO_y was highest when boundary layer isoprene was $>$500 ppt both because NO_y was lower and ΣANs were higher in those regions. Evidence was presented to indicate that the measured hydrocarbon suite was reasonably comprehensive and calculations based on the observed hydrocarbons indicate that isoprene was the main precursor to organic nitrates not only when isoprene was especially high but in the complete set of boundary layer continental data. A strong correlation was observed between ΣANs and CH_2O, a high-yield product of isoprene oxidation, and this was used to constrain uncertainties in both the nitrate yield from OH-initiated isoprene oxidation and in the loss processes governing the resulting hydroxy nitrates. The data presented here constrain combinations of branching ratios and lifetimes and show that the extent to which the nitrate functionality is maintained through the second generation of isoprene oxidation products is at least 75%. Observations of ΣANs, O_3, hydrocarbons and speciated nitrates are in best agreement when isoprene nitrate branching ratios are at the lower end of the published range of values (4.4–12%). We find combinations of production rates, lifetimes and recycling efficiencies of INs that are equally good fits of the data as follows (4.4%, 16 h, 97%), (8%, 2.5 h, 79%) and (12%, 95 min, 67%). Regardless of the initial branching ratio, the data imply a high nitrate recycling efficiency for INs. None of the models commonly used to describe ozone in regions where isoprene is important represent this chemistry in sufficient detail to capture the effects of these mechanistic relationships on O_3 or aerosol production. Improving the mechanisms in these models as well as through laboratory observations will lead to more realistic assessments of the combined effects of isoprene and NO_x on O_3, SOA production and nitrogen deposition.

Acknowledgements. The analysis described here was funded by NASA grants NNG05GH196 and NAG5-13668 and by NASA headquarters under the NASA Earth and Space Science Fellowship Program. The authors would also like to sincerely thank the NASA DC8 flight and ground crews for invaluable logistical support, the DC8 science team for an incredibly creative and rewarding collaboration and especially Melody Avery for editorial input.

Edited by: V. Faye McNeill

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